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Selected Energy Epitaxial Deposition and Low Energy Electron Microscopy of AlN, GaN and SiC Thin Films

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13. ABSTRACT *(Maximum 200 words)*

Epitaxial growth GaN films at reasonable rates and at grazing incidence and using conditions similar to those employed for growth in a low energy electron microscope (LEEM) have been achieved. Preliminary phtoluminescence studies showed near band edge luminescence accompanied by yellow luminescence at ~2.2 eV. *In situ* experiments in the LEEM at ASU to produce a clean GaN substrate surface for homoepitaxy were performed. Heating the substrate to 880°C produced a (1×1) structure with meandering steps on the surface. Cleaning the substrates using a N-atom flux produced different atomic structures depending on the N-atom flux and the substrate temperature. Low N-atom flux gave rise to a structure with clear steps while a higher N-atom flux produced a (3×3) surface with vanishing steps. Growth of GaN on the (3×3) surface produced faceted layers. Additional *in situ* cleaning research at NCSU of MOCVD-grown GaN/AlN/6H-SiC substrates using NH_3-seeded supersonic molecular beams was investigated. Surface carbon and oxygen concentrations of ~1%, as evidenced by XPS, were achieved by heating at 730°C under a hyperthermal NH_3 flux. Oxygen was removed primarily by thermal desorption. In contrast, carbon removal required heating under an NH_3 flux. *Ex situ* AFM reveals a smooth surface with parallel steps after NH_3 beam cleaning. Homoepitaxial growth of smooth, highly textured GaN films was accomplished at 700°C by employing a hyperthermal NH_3 beam (0.61 eV) and an effusive Ga source.

14. SUBJECT TERMS
GaN, gallium nitride, epitaxy, films, low energy electron microscope, LEEM, phtoluminescence, cleaning, N-atom flux, supersonic molecular beams, carbon, oxygen, NH_3 flux, hyperthermal

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I. Introduction

The realized and potential electronic applications of AlN, GaN and SiC are well known. Moreover, a continuous range of solid solutions and pseudomorphic heterostructures of controlled periodicities and tunable band gaps from 2.3 eV (3C-SiC) to 6.3 eV (AlN) have been produced at North Carolina State University (NCSU) and elsewhere in the GaN-AlN and AlN-SiC systems. The wide band gaps of these materials and their strong atomic bonding have allowed the fabrication of high-power, high-frequency and high-temperature devices. However, the high vapor pressures of N and Si in the nitrides and SiC, respectively, force the use of low deposition temperatures with resultant inefficient chemisorption and reduced surface diffusion rates. The use of these low temperatures also increases the probability of the uncontrolled introduction of impurities as well as point, line and planar defects which are likely to be electrically active. An effective method must be found to routinely produce intrinsic epitaxial films of AlN, GaN and SiC having low defect densities.

Recently, Ceyer [1, 2] has demonstrated that the barrier to dissociative chemisorption of a reactant upon collision with a surface can be overcome by the translational energy of the incident molecule. Ceyer's explanation for this process is based upon a potential energy diagram (Fig. 1) similar to that given by classical transition-state theory (or activated-complex theory) in chemical kinetics. The dotted and dashed lines in Fig. 1 show, respectively, the potential wells for molecular physisorption and dissociative chemisorption onto the surface. In general, there will be an energy barrier to overcome for the atoms of the physisorbed molecule to dissociate and chemically bond to the surface. Depending upon the equilibrium positions and well depths of the physisorbed and chemisorbed states, the energy of the transition state E^* can be less than zero or greater than zero. In the former case, the reaction proceeds spontaneously. In the latter case, the molecule will never proceed from the physisorbed state (the precursor state) to the chemisorbed state unless an additional source of energy can be drawn upon to surmount the barrier. This energy can only come from either (1) the thermal energy of the surface, (2) stored internal energy (rotational and vibrational) of the molecule, or (3) the incident translational kinetic energy of the molecule. Conversion of translational kinetic energy into the required potential energy is the most efficient of these processes. Moreover, by adjusting the kinetic energy, Ei, of the incoming molecule, it is possible to turn off the reaction ($Ei < E^*$), to tailor the reaction to just proceed ($Ei = E^*$), or to set the amount of excess energy to be released ($Ei > E^*$). The thrust of the present research is to employ these attributes of the beam translational energy to tune the reaction chemistry for wide band gap semiconductor epitaxial growth.

The transition state, E^*, is essentially the activation energy for dissociation and chemisorption of the incident molecules. Its exact magnitude is unknown, but is most certainly

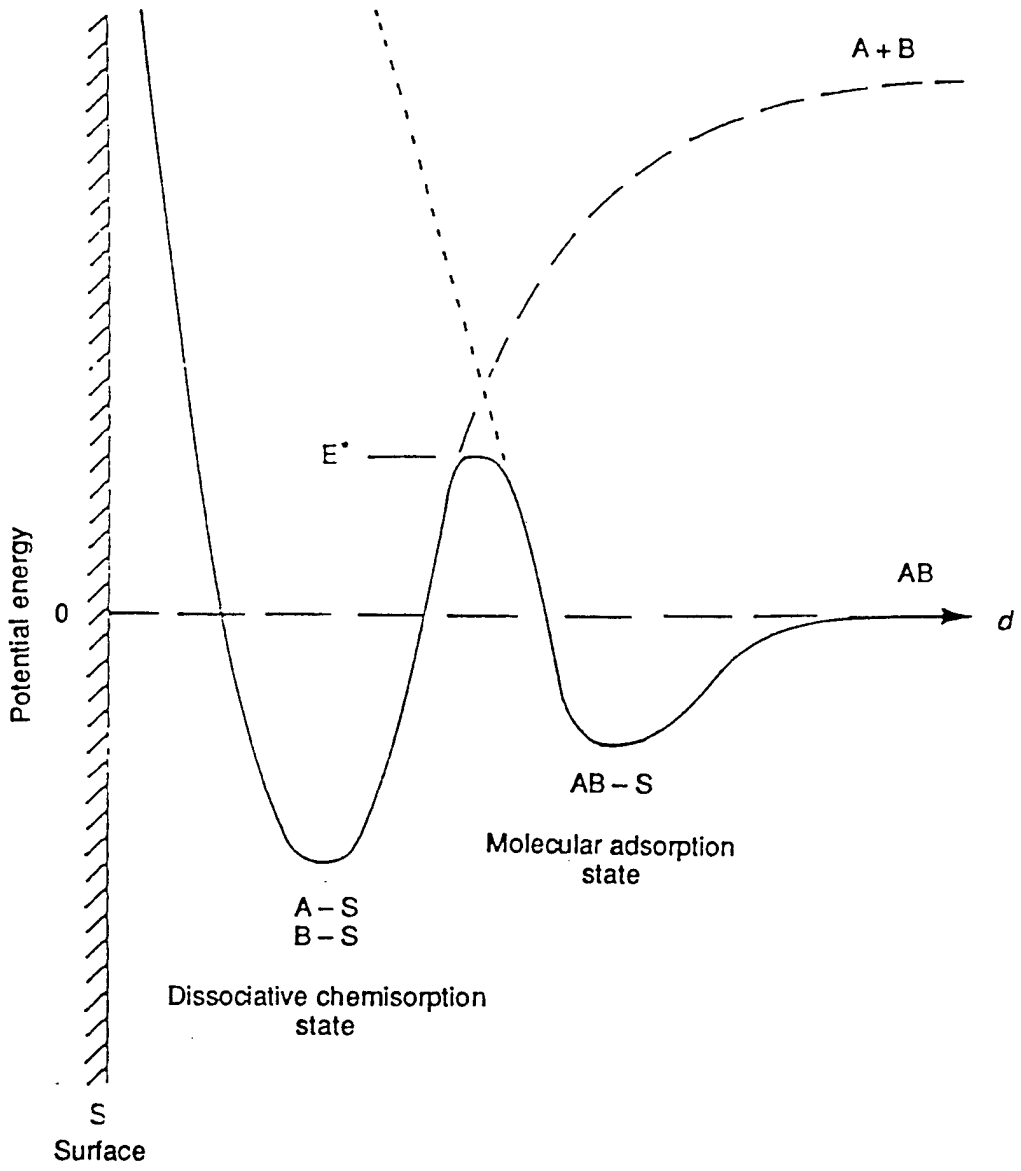

Figure 1. Schematic potential energy diagram of an activated surface reaction involving a molecularly physisorbed precursor state [from Ref. 1].

lower than the dissociation energy of the free molecule. It does not necessarily follow, however, that any kinetic energy above E* will promote high-quality epitaxial growth of GaN. One must take into consideration another energy threshold, Ed, beyond which the kinetic energy of the incident flux will cause damage to the epitaxial film being synthesized. A typical Ed threshold value is approximately five times the bandgap of the crystal and in the case of GaN, Ed ≈18 eV.

From the above consideration, it is clear that the key to high quality epitaxial growth is to be able to tune the energy of the incoming flux species over a range of energies defined by the window between E* and Ed. Since the window is quite restrictive, i.e. 1-20 eV, it is essential that the energy spread of the flux species must be small, i.e. the flux species should ideally be

monoenergetic. To this end, we employ selected energy epitaxial deposition (SEED) systems for the growth of AlN, GaN and SiC wide band gap semiconductors. The SEED systems are of two types: (1) a seeded-beam supersonic free-jet (SSJ) and (2) a dual ion-beam Colutron. Both these SEED systems have the desirable property of a narrow energy spread of ≤ 1 eV.

Epitaxial growth using the seeded-beam SSJ involves a close collaboration between investigators at NCSU and Arizona State University (ASU). At ASU, the SSJ is interfaced directly into a low-energy electron microscope (LEEM) for the conduct of *in situ* studies of the nucleation and growth of epitaxial layers; while at NCSU, the SSJ systems are used to grow device-quality AlN, GaN and SiC for real applications. Exchanges in personnel (students) and information between the two groups ensures the achievement of desired results. The additional thin film growth experiments using dual-beam Colutrons and the theoretical studies referred to in this report are primarily conducted at ASU.

The research conducted in this reporting period and described in the following sections has been concerned with (1) epitaxial growth GaN films at reasonable rates and at grazing incidence and using conditions similar to those employed for growth in a low energy electron microscope (LEEM) and their characterization, (2) *in situ* experiments in the LEEM to produce a clean GaN substrate surface for homoepitaxy, (3) the investigation of additional GaN substrate cleaning techniques, and (4) homoepitaxial growth of GaN films using ammonia-seeded supersonic beams. The following individual sections detail the procedures, results, discussions of these results, conclusions and plans for future research. Each subsection is self-contained with its own figures, tables and references.

1. S. T. Ceyer, Langmuir 6, 82 (1990).
2. S. T. Ceyer, Science 249, 133 (1990).

II. Effects of Energy and Angle of Incidence on AlN and GaN Epitaxial Growth using Helium Supersonic Beams Seeded with NH_3

A. Introduction

The nitride family of AlN, GaN and InN thin films have shown to be strong candidates for electronic and optoelectronic applications. With direct band gaps of 6.2 eV, 3.4 eV and 1.9 eV for AlN, GaN and InN respectively, solid solutions based on these materials provide for band gap modifications suitable for applications ranging from the red to the deep UV region of the spectrum [1]. Due to the high bond strength between N and H in NH_3, the growth of III-V nitrides requires high substrate temperatures unless some other form of activation is present. Supersonic molecular beam epitaxy (SMBE) has been shown to enhance the surface decomposition of silane and methane [2,3] because of the possibility of tuning the kinetic energy of these species to deform and cleave the bonds upon impact with the substrate. In addition, the tuning of the energy spread is possible with SMBE. This is important in order to experimentally determine the chemisorption barriers for the systems being studied, as well as to provide species with high sticking coefficients at high enough intensities. Supersonic molecular beam epitaxy is, therefore, a useful technique for the low-temperature growth of single-crystalline GaN films at suitable growth rates using NH_3. A review of supersonic molecular beams can be found in Scoles [4].

Growth of stoichiometric, smooth epitaxial AlN and GaN films on 6H-SiC(0001) was accomplished using He supersonic beams seeded with NH_3. The dependence of the film properties on the kinetic energy and angle of incidence of the beam with respect to the surface normal of the substrate was studied. The optical properties of the films were investigated.

B. Experimental Procedure

The deposition chamber used for the current deposition experiments is the same deposition chamber used for previous MBE work at ASU [Sept. 97 Progress Report]. The samples were resistively heated by passing a current through them and the temperature was measured using a disappearing filament pyrometer. The temperatures of the Al and Ga evaporators were also measured with the pyrometer and set at 1110°C and 1010°C, respectively. In the present study, the substrates were on-axis 6H-SiC(0001) purchased from Cree Research, Inc. The substrates were degreased by rinsing in methanol, acetone and isopropanol at 60°C for five min. The substrates were then sonicated in DI water for five min. followed by a dip in a 10% HF aqueous solution for fifteen min. An alternate substrate preparation procedure consisting of an exposure to a 5% hydrogen in helium mixture at 1600°C for fifteen minutes was also utilized. It has been shown [Dec. 97 progress report] that this treatment leads to a scratch free surface with flat terraces. Growth was performed on substrates prepared by both techniques.

After preparation, the samples were loaded into the deposition chamber and the chamber was evacuated and baked such that a base pressure < 8×10^{-9} Torr is obtained. A liquid nitrogen trap was then filled to obtain a base pressure < 7×10^{-10} Torr. The evaporators were degassed by gradually heating them to the operating temperatures while maintaining a pressure of < 1×10^{-8} Torr. The sample was then degassed by heating to ~ 500°C while the pressure in the chamber was maintained at < 5×10^{-9} Torr. The samples were then annealed at 900°C for 20 min. At this point, the isolation valve between the source chamber and the deposition chamber was opened such that the NH_3 seeded He beam impinged on the sample. The NH_3 flux was 3.5×10^{14} $cm^{-2}s^{-1}$. The shutter on the Al evaporator was also opened and growth of AlN was performed for 60 min. After the deposition of AlN was completed, the samples were set at 800°C and the Ga evaporator was opened. Deposition of GaN was performed for 60 min. The films were characterized using Auger electron spectroscopy (AES), Rutherford back-scattering spectroscopy (RBS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL), electron channeling patterns (ECP) and atomic force microscopy (AFM).

C. Results

The Ga and Al evaporators were calibrated using a Maxtek TM-100R quartz crystal oscillator. The fluxes for various currents are shown in Table I. The Al and Ga fluxes for the experiments done at normal incidence were 2.5×10^{14} $cm^{-2}s^{-1}$ and 6.22×10^{14} $cm^{-2}s^{-1}$, respectively. The fluxes were adjusted accordingly when the angle of incidence was change.

Some of the work on the effect of kinetic energy and angle of incidence on the growth rate of the GaN layers has been reproduced during the last three months. The duplicate set of films produced during this period are being analyzed. Preliminary results support the trends we reported in the last progress report [Dec. 1997]. In addition to this work, it has been observed that grazing angles of incidence (i.e. 15°, which is the angle of incidence in the LEEM experiments) do not present a problem as far as growth is concerned. The film thickness obtained under these conditions was 350 Å. The film thickness obtained was comparable to films grown at normal incidence with the same fluxes.

Further characterization of the films was performed. AFM analysis showed very similar surface morphologies for AlN layers grown on "as-received" and hydrogen etched substrates. TEM analysis is being performed to asses the cause for the marked difference in the value of the RBS minimum yield measurements for such layers. A complete analysis of the layers will be available in the following three months.

Preliminary PL spectra of our films display room temperature near band edge luminescence at 3.42 eV (Fig. 1). The spectra shows the yellow luminescence band at ~ 2.2 eV which has

Table I. Evaporation Fluxes for Al and Ga Evaporators

Element	Density (g-cm^{-3})	Current (A)	Flux (cm^{-2}-s^{-1})
Ga	5.93	14.0	0.55×10^{14}
Ga	5.93	15.0	1.87×10^{14}
Ga	5.93	16.0	6.22×10^{14}
Al	2.70	19.0	0.50×10^{14}
Al	2.70	20.2	2.50×10^{14}

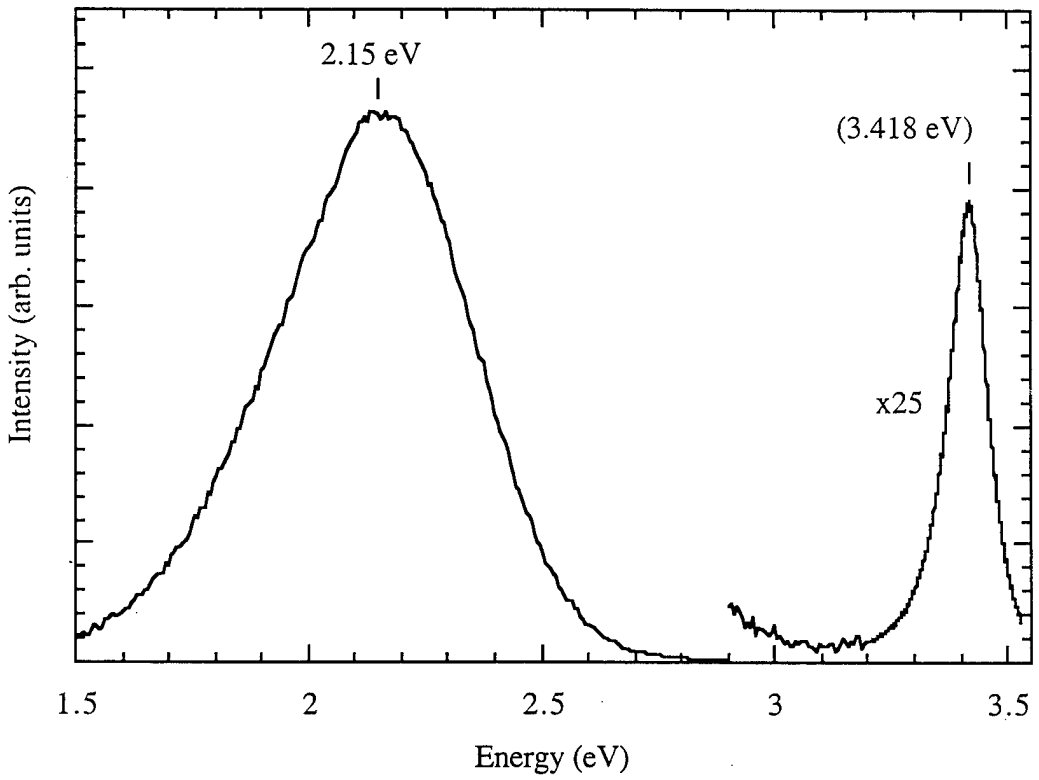

Figure 1. Room temperature photoluminescence spectra exhibiting near band edge luminescence at 3.418 eV.

been observed extensively in GaN films. It is possible that the yellow luminescence is due to defects associated with dislocations. This has been proposed as an explanation for the origin of the yellow luminescence by Lee *et al.* [5] and Liu *et al.* [6]. However, there is no clear and unique explanation for it. The high dislocation density (i.e. ~ 1×10^{10} cm^{-2}) of our films can be

explained by the film thickness (i.e. 2000 Å). Weeks *et al.*[7] has shown that the GaN dislocation density decreases rapidly within a micron from the AlN interface. It is important to point out that the attainment of near band edge luminescence attest to the high quality of the films even though they are thin.

D. Conclusions

The experiments presented in the last progress report [Dec. 97] have been reproduced. These films are being analyzed at the present time. Growth was performed at grazing incidence, similar to LEEM conditions, and found that epitaxial growth at reasonable growth rates is possible. Preliminary PL shows near band edge luminescence accompanied by yellow luminescence at ~ 2.2 eV.

E. Future Work

Further film characterization will be carried out to insure the reproducibility of the trends presented in the last progress report [Dec. 97]. TEM characterization of the defect structure of AlN films grown on "as-received" and hydrogen etched substrates will be completed. The connection of the supersonic molecular beam source with the LEEM will be pursued.

F. References

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III. LEEM/LEED Studies of GaN Homoepitaxy on GaN Substrates

In situ experiments have been conducted in the LEEM to produce a clean GaN substrate surface for homoepitaxy. Heating the substrate to 880°C produced a (1×1) structure with meandering steps on the surface. Cleaning of the substrates by an N-atom flux produced different atomic structures depending on the N-atom flux and the substrate temperature. Low N-atom flux gave rise to a $\left(\sqrt{3} \times \sqrt{3}\right)$ structure with clear steps while a higher N-atom flux produced a (3×3) surface with vanishing steps. Growth of GaN on the (3×3) surface produced faceted layers.

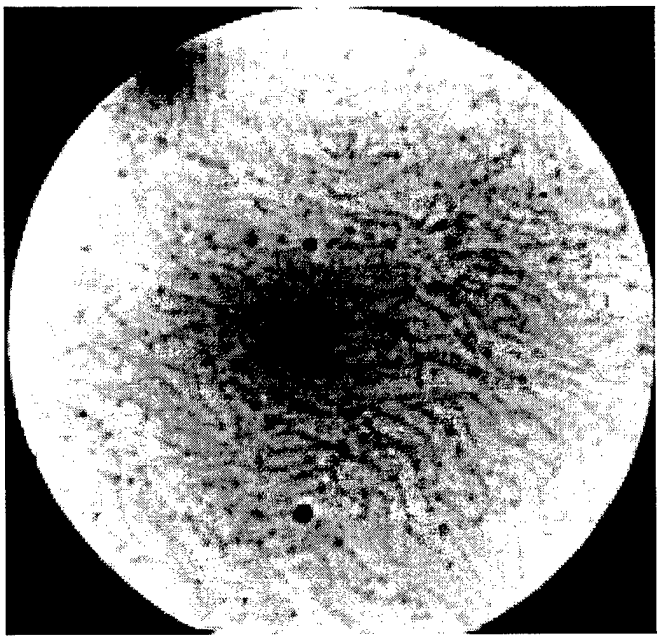
LEEM/LEED studies have been conducted on four GaN substrates grown by MOCVD on SiC supplied by Davis' group at North Carolina State University. The objectives are to establish cleaning procedures for these substrates and deposition parameters for GaN homoepitaxy on these substrates. The thickness of the MOCVD GaN substrates was 3 μm.

Figure 1 shows the cleaning of a GaN substrate by heating only. Upon heating to 650°C, the LEEM image of the surface, Fig. 1(a), shows random meandering steps. The LEED pattern in Fig. 1(b) shows a clear (1×1) structure of the basal plane of GaN (0001). This surface was stable to 880°C, above which the steps vanished and the LEEM image showed a grainy surface. The LEED pattern developed facet spots and the (00) spot disappeared indicating that the basal plane was not longer stable and pyramidal facets developed on the surface.

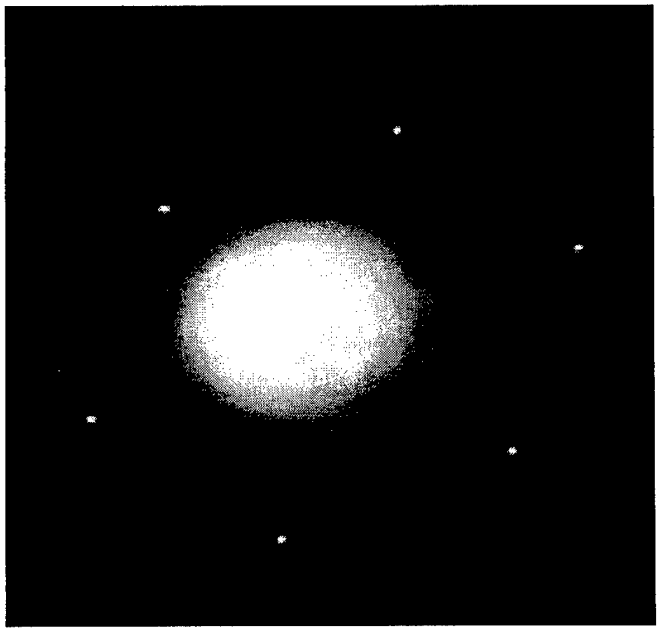
Cleaning of the GaN substrate by a flux of N atoms from an EPI RF plasma source resulted in the LEEM image shown in Fig. 2(a). The N-atom flux was 0.25 ML/min and the substrate temperature was held at 675°C. After 30 min of the N-atom cleaning treatment, the LEED pattern shows clear $\left(\sqrt{3} \times \sqrt{3}\right)$ spots in addition to the (1×1) spots as shown in Fig. 2(b). No significant change was observed after 90 min of the N-atom cleaning treatment. Ga metal was deposited on this surface to investigate the polarity of the GaN layer. A pseudo (1×1) structure with satellite spots was observed, which probably corresponded to a Ga terminated layer.

A GaN substrate was cleaned with a N-atom flux of 0.35 ML/min at 720°C. After 7 min, steps appeared in the LEEM image and the LEED pattern showed (1×1) spots. After a further 30 min of cleaning treatment, the (1×1) spots became stronger and weak spots of a (3×3) structure appeared as shown in Fig. 3(b). At 60 min, the (3×3) spots became more intense as shown in Fig. 3(c), but the LEEM image in Fig. 3(a) showed a weaker contrast of the surface with the step structure disappearing. Growth of GaN was conducted on this (3×3) surface at 680°C with the N flux increased to 0.50 ML/min and the Ga flux at 1 to 3 ML/min. After two hours of deposition, the LEED pattern developed facet spots as shown in Fig. 4 while the LEEM image showed a grainy surface indicating the growth of a faceted GaN layer.

Future work will include homoepitaxial growth of GaN on GaN substrates with well-defined polarity. The (3×3) surface is most likely N-terminated (Feenstra, SEE-3 Workshop) while the $\left(\sqrt{3} \times \sqrt{3}\right)$ is Ga-terminated.

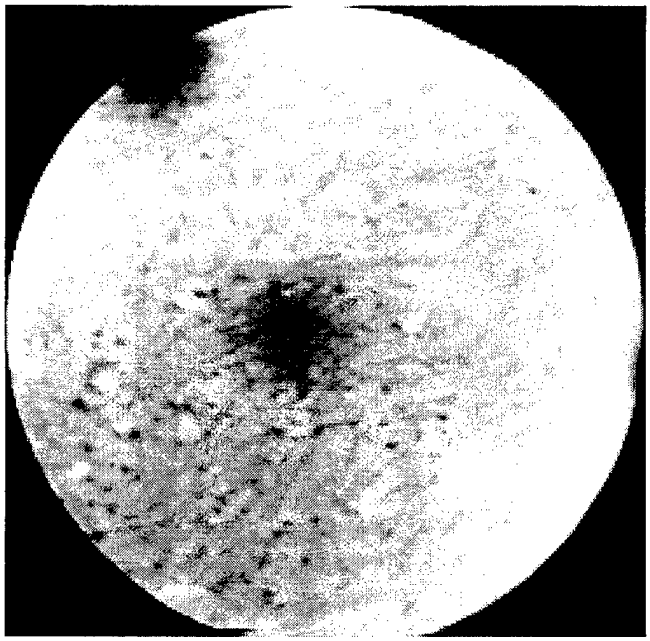


(a)



(b)

Figure 1. GaN layer cleaned by annealing at 650°C: a) LEEM image, energy 12 eV, field of view 4.8 μm; b) LEED pattern at 22.8 eV.



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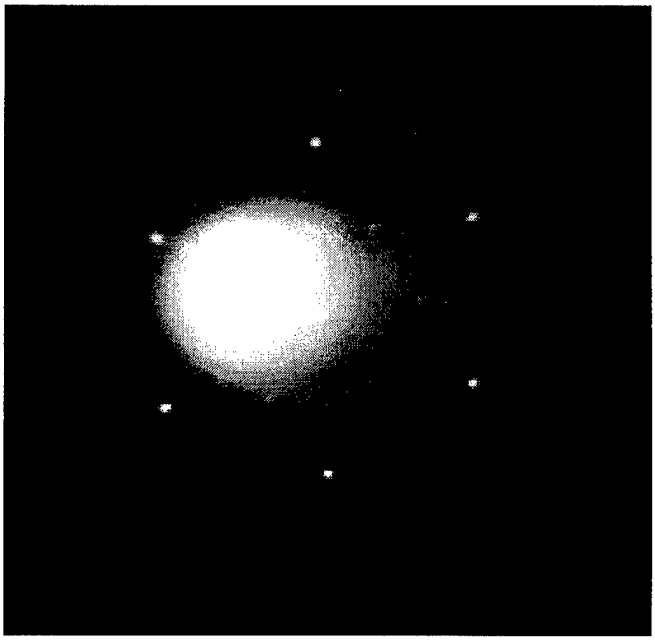
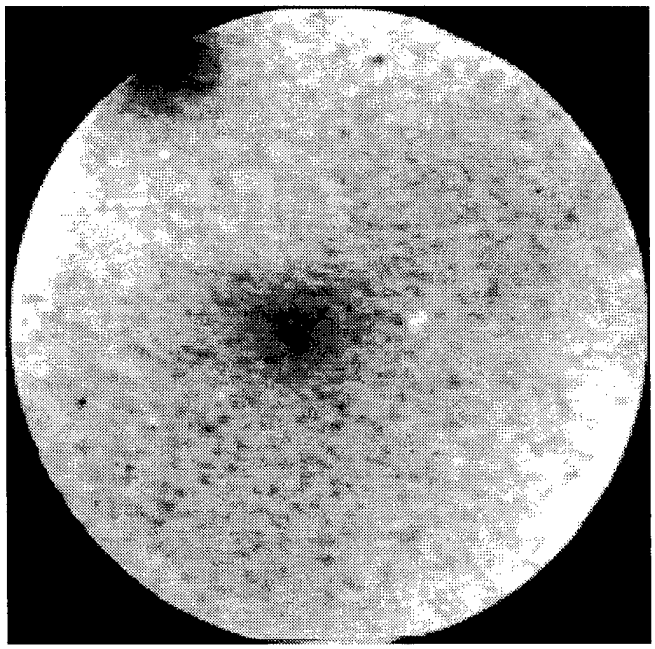


(b)

Figure 2. GaN layer cleaned by atomic nitrogen at 675°C: a) LEEM image, energy 12 eV, field of view 4.8 μm; b) LEED pattern at 32.8 eV.



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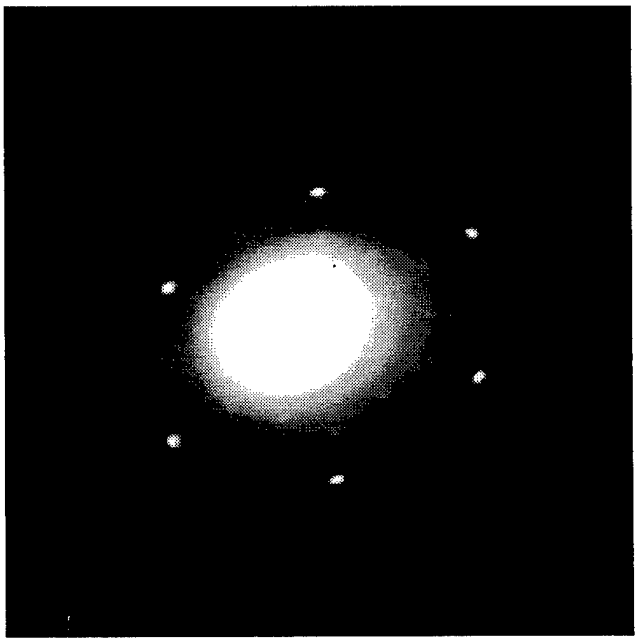

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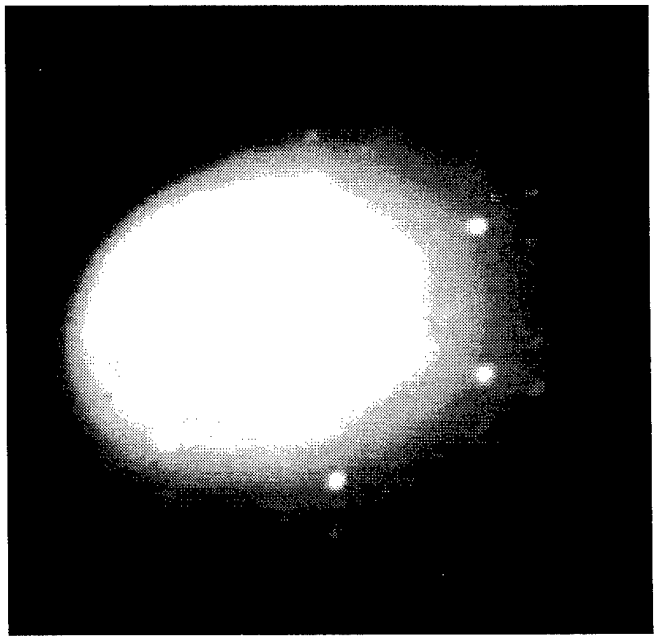
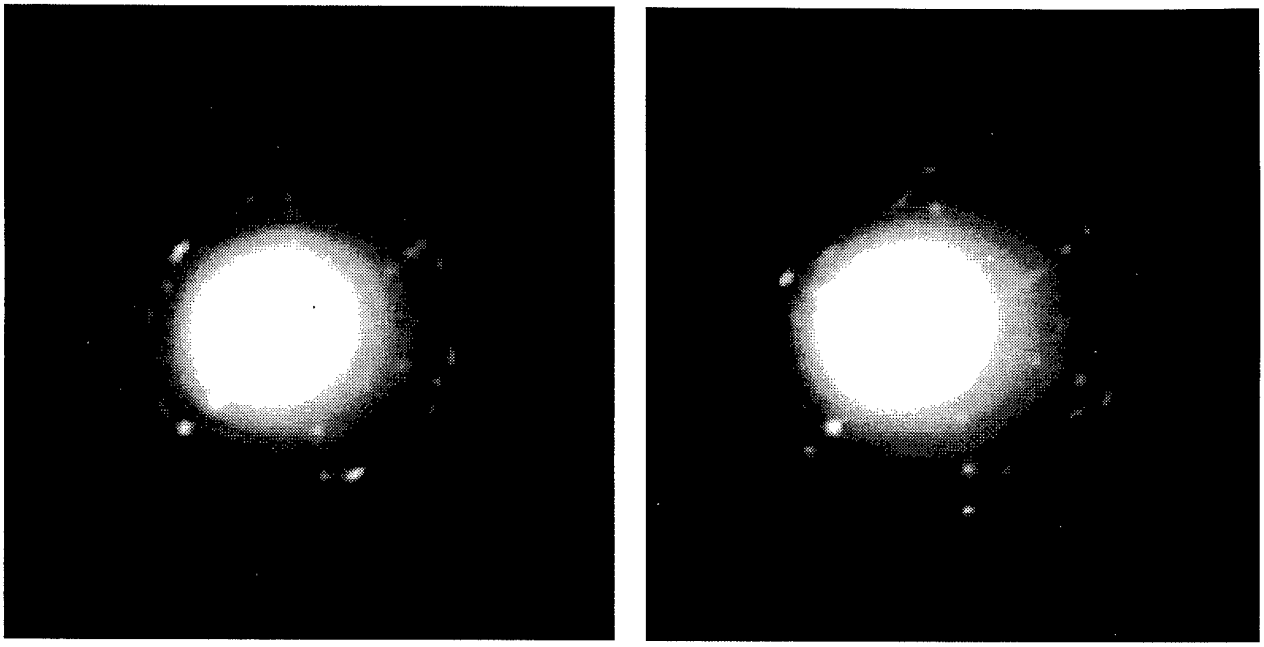


(c)

Figure 3. GaN layer cleaned by atomic nitrogen at 720°C: a) LEEM image at 12 eV, field of view 4.8 μm; b) LEED pattern at 18.8 eV(b) and 44.0 eV(c).



(a) (b)

Figure 4. LEED pattern of homoepitaxially grown GaN layer: (a) 18.6 eV (b) 22.5 eV.

IV. *In Situ* Cleaning and Homoepitaxial Growth of GaN Films Using an Ammonia-seeded Supersonic Beam

A. Introduction

Gallium nitride is a wide bandgap semiconductor (Eg=3.4 eV) with many potential optoelectronics and high-temperature, high-frequency, microelectronics applications. GaN forms a continuous range of solid solutions with AlN (6.28 eV) and InN (1.95 eV), permitting the fabrication, via bandgap engineering, of laser diodes with tunable emission frequencies from covering the visible and UV regions. State-of-the-art GaN films ($\leq 10^8$ defects per cm^2) have been used to fabricate blue light emitting diodes (LEDs) and laser diodes.

Heteroepitaxial growth of high-quality monocrystalline GaN films has been problematic due to the lack of a suitable lattice-matched substrate and the thermodynamic instability of GaN under high-temperature growth conditions. Sapphire, the most common substrate, exhibits a 14% lattice mismatch at the GaN(0001)/sapphire(0001) interface; moreover, the thermal expansion coefficient of sapphire is 25% greater than that of GaN. Only by employing a low-temperature AlN or GaN buffer layer can one obtain monocrystalline GaN films on sapphire with defect densities in the 10^8-10^9 cm^{-2} range.

Substrate temperatures in excess of 1000°C are employed for growth of monocrystalline GaN films by halide or metal-organic CVD (MOCVD) using NH_3. In MOCVD, substrate thermal energy is used to overcome activation barriers for precursor decomposition and adatom surface migration (lateral diffusion); however, GaN decomposition above 620°C *in vacuo* necessitates the use of large V/III flux ratios [1]. Plasma-assisted processes have been utilized to lower the GaN growth temperature to approximately 700°C, but ion-induced damage and oxygen contamination are often observed.

The use of energetic neutral beams of precursor molecules is an alternative approach to the epitaxial growth of GaN films at lower substrate temperatures. In selected energy epitaxy (SEE), heavy reactant molecules are seeded in a supersonic expansion of light molecules and thereby accelerated to hyperthermal energies. The precursor molecules attain kinetic energies on the order of 1-2 eV which can provide the necessary energy for activated surface processes, such as dissociative chemisorption and adatom migration. Hence, in prospect, monocrystalline GaN films may be grown at lower substrate temperatures by SEE than by conventional MOCVD [2]. Moreover, energetic neutral beams with narrow energy distributions are ideal tools for fundamental studies of wide band gap semiconductor growth using *in situ* low-energy electron microscopy (LEEM) and other techniques.

To demonstrate the potential advantages of SEE, homoepitaxial growth of GaN on high-temperature MOCVD-grown GaN substrates is under investigation. This approach obviates the substrate lattice-mismatch issue, allowing the effects of precursor kinetic energy and film

morphology to be studied in isolation. It has become increasingly apparent, however, that in order to achieve 2-D, step flow growth methods for *in situ* surface cleaning must be perfected. In this report, detailed results of *in situ* GaN substrate cleaning using a seeded supersonic NH_3 beam are presented, and the effects of substrate cleaning on homoepitaxial growth using a seeded supersonic NH_3 beam and Ga effusion cell are illustrated.

B. Experimental Procedure

SEED/XPS Deposition System. The SEED/XPS multi-chamber system described in previous reports (June 1996, Dec. 1996) was used for homoepitaxial growth of GaN. The orifice used in the NH_3 nozzle was 150 mm. A conical skimmer used for extracting the NH_3 beam from the supersonic free jet has an opening of 1 mm in diameter, a base of 20 mm in diameter, an included angle of 25° at the opening and of 70° at the base, and a height of 17 mm. The collimation aperture of 5×5 mm^2 is located downstream between the 2nd differential pumping stage and the growth chamber. The molecular beam is directed to the substrate with an incident angle of 6° with respect to the surface normal. The deposition area on the vertical substrate is 15×15 mm^2.

Substrate Preparation/Cleaning. The substrates were 0.5-μm thick GaN films grown by MOVPE on on-axis 6H-SiC employing a 0.1-μm thick AlN buffer layer. The substrates were provided by Prof. Davis' group and used as received. Ag paste is used to provide good thermal contact between the Mo sample holder and the GaN/AlN/6H-SiC substrate; two Mo pins are used to hold the substrate in place. The Mo holder is placed on a hot plate to dry the Ag paste for 5 min at 80°C. Subsequently, it is introduced via the load-lock chamber and transferred *in vacuo* into the growth chamber. The sample is heated slowly to 400°C under an NH_3 flux for outgassing. Prior to the growth, the GaN substrate is cleaned *in situ* by NH_3 beam exposure at 730°C for 30 min, unless otherwise noted. After *in situ* cleaning the substrate temperature is lowered to 200°C under an NH_3 flux. The GaN substrate is examined by RHEED before and after *in situ* cleaning, as well as XPS to determine the surface carbon and oxygen contamination.

Homoepitaxial Growth Using Supersonic NH_3 Beam and Ga Effusion Cell. A hot-lip Ga Knudsen cell (K-cell) described in a previous report (June 1997) was used for the homoepitaxial growth of GaN. Films were grown using the Ga cell and a NH_3-seeded supersonic molecular beam. Growth was initiated by opening the K-cell shutter after both the Ga crucible and the substrate were at the desired temperatures. Growth runs lasted for two hours, unless otherwise noted. Many of the growth experiments were with the NH_3 nozzle heated to 200°C and the stagnation pressure in the 745-755 Torr range, employing a NH_3 flow rate of 60 sccm and a He flow rate of 200 sccm. Changes in the NH_3 kinetic energy were made by changing the nozzle temperature, 25°C-600°C, or the NH_3 flux, 30 or 60 sccm. Gallium

nitride growth experiments were with substrate temperature of 700°C and Ga K-cell temperature of 950°C. Growth rates were determined by profilometer measurement of the step height of the film created by the pins holding the substrate, and it was referenced to the cross sectional SEM images.

XPS Analysis. The UHV surface analysis chamber was equipped with a PHI 3057 XPS system comprising a 10-360 spherical capacitor analyzer (SCA), Omni Focus III fixed-aperture lens, 16-element multichannel detector, and 257 DR11 PC interface card. A PHI 1248 dual-anode (Al/Mg) X-ray source was used. The sample was mounted on a tilt stage which was attached to a precision *xyz*-rotary manipulator (Thermionics). The analysis chamber was pumped by a Perkin-Elmer TNBX ion pump/TSP combination and had a base pressure of 8×10^{-11} Torr. After growth, samples were transferred to the XPS chamber through vacuum transfer lines. XPS spectra were taken with both Mg and Al anodes to isolate N(1s), O(1s), C(1s) and Ga($2p_{3/2}$) photoelectron peaks from other interfering signals.

RHEED Analysis. In situ reflection high-energy electron diffraction (RHEED) measurements were made using a Fisons LEG 110 15-kV electron gun and 100-mm Al-coated phosphor screen. RHEED patterns of the GaN substrate before and after the *in situ* cleaning, and after GaN growth were taken at 15kV.

SEM Analysis. Scanning electron microscope images of GaN films were obtained using a JEOL 6400FE SEM with a 5-kV cold field emission electron gun. Both surface and cross sectional images were taken.

AFM Analysis. The AFM images were obtained using a Digital Instruments Dimension 300 Scanning Probe Microscope with a Nanoscope IIIa Controller. A silicon tip with a nominal tip radius of curvature of 5-10 nm was used.

C. Results and Discussion

In situ Substrate Cleaning Using a Seeded Supersonic NH_3 Beam. GaN substrates were cleaned using various NH_3 beam conditions, cleaning temperatures and cleaning times. The surface of the as-received substrates contain 9-14% oxygen and 12-19% carbon contamination, as evidenced by XPS. The *in situ* cleaning results are detailed in Table I. XPS analysis of films cleaned at 850°C indicate decomposition of the substrate. Oxygen contamination can be removed thermally with substrate temperatures as low as 730°C. The effects of heating under an NH_3 beam on contaminant removal are highlighted in the XPS spectra in Fig. 1.

Heating the samples to 730°C *in vacuo* removes most of the oxygen (2%) but very little of the carbon (9%). The O (1s) binding energy after *in situ* cleaning is similar to that of Ga_2O_3 (530.8 eV), so we infer that the oxygen remaining on the surface after *in situ* cleaning is bonded to the Ga. The removal of carbon contamination necessitates the use of NH_3. It is

Table I. Surface Carbon and Oxygen Concentrations for Different GaN *In Situ* Cleaning Conditions

Substrate Temperature (°C)	% NH_3/ NH_3 KE (eV)	Cleaning Time (min)	%C	%O
800	23% / 0.25 eV	15	7	3
730	23% / 0.25 eV	30	4	3
730	no NH_3	30	9	2
730	heat *in vacuo* (30 min) 23% / 0.25 eV	30	1	1
730	10% / 0.33 eV	60	4	5
730	10% / 0.61 eV	60	4	6

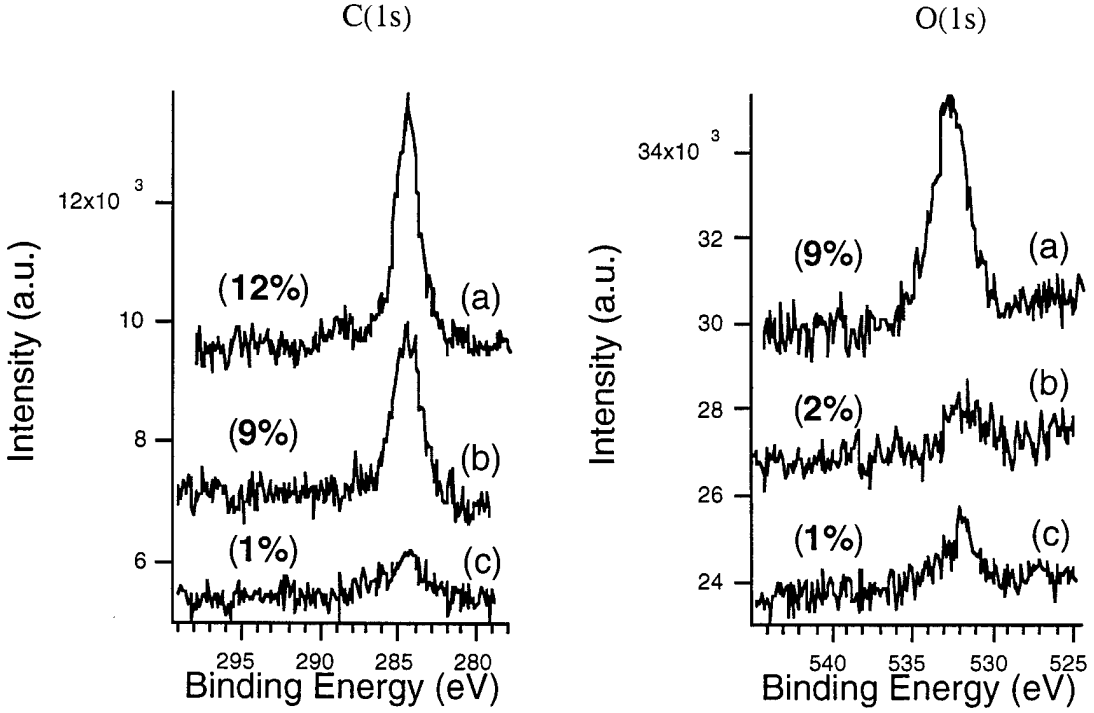


Figure 1. XPS Results of carbon and oxygen removal from GaN at 730°C:
(a) GaN substrate before cleaning,
(b) after heating *in vacuo* at 730°C for min,
(c) after subsequent heating under an NH_3 beam at 730°C for 30 min.

proposed that organic contaminants are removed via the formation of volatile hydrocarbons by reaction with H atoms supplied by NH_3 decomposition. As seen in Table I, changes in cleaning time, NH_3 flux and kinetic energy do not significantly affect the removal of contaminants.

NH_3 beam cleaning at 730°C does not destroy the stepped surface of the GaN substrate and is successful in making the substrate smoother as evidenced by *in situ* RHEED and *ex situ*

AFM. A streaky, 1×1 RHEED pattern with Kikuchi lines typically was obtained from the as-received substrate. A similar 1×1 pattern with sharper lines and lower background intensity was found after NH_3 beam exposure at 730°C for 30 min. This result indicates removal of surface contaminants without surface reconstruction. An AFM comparison of the GaN surface morphology before and after cleaning is shown in Fig. 2.

AFM of the substrate before cleaning shows a stepped surface with many small protrusions. Heating under a 0.33 eV NH_3 beam removes the small protrusions and does not destroy the surface steps. The RMS roughness of the as-received substrate was reduced from 0.33 to 0.20 nm after *in situ* cleaning. The surface morphology after cleaning does not change with NH_3 beam conditions; a stepped surface with an RMS roughness of 0.26 nm was found for a surface cleaned with a 0.6 eV NH_3 beam.

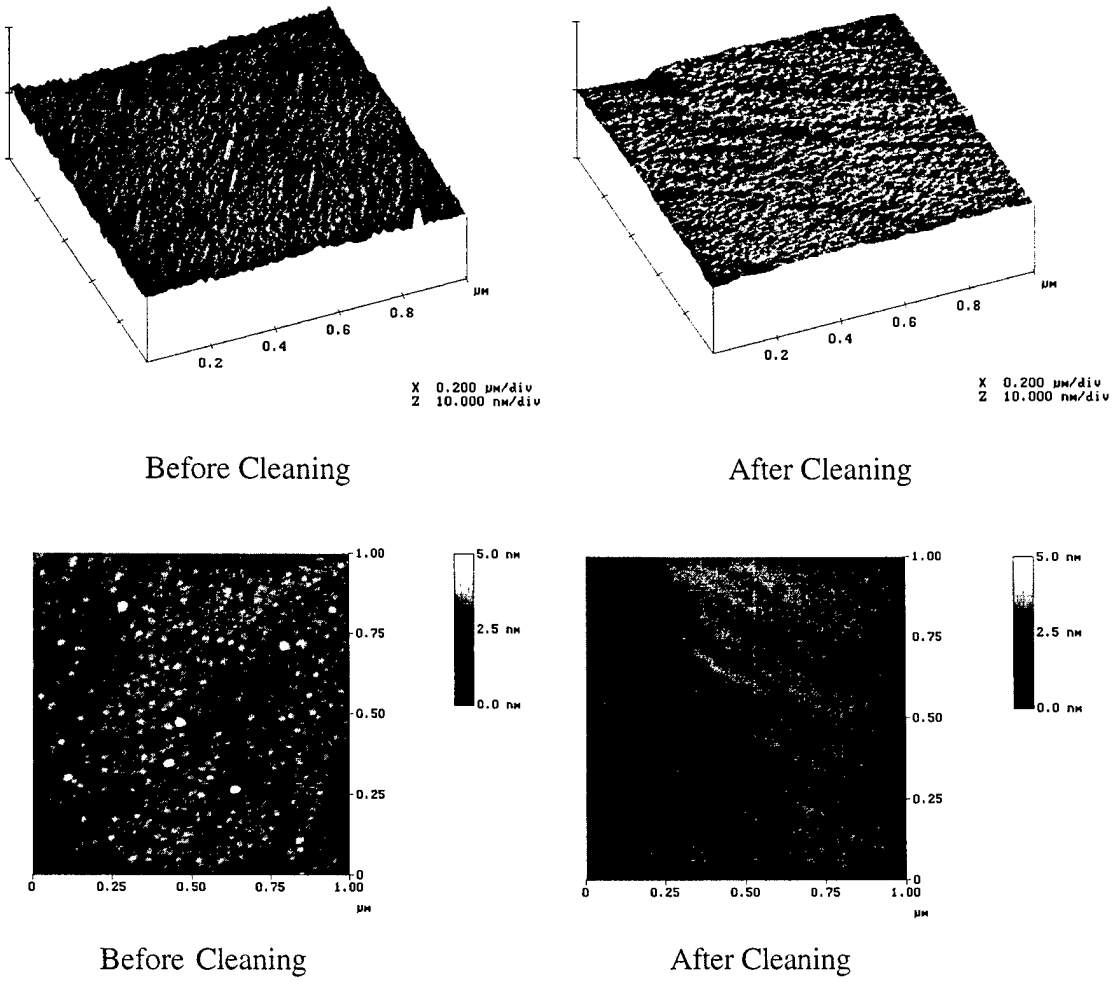


Figure 2. Inclined and top-view AFM images of a 0.5 μm GaN substrate before and after NH_3 cleaning at 730°C for 30 min.

Homoepitaxial Growth Using Supersonic NH_3 Beam and Ga K-cell. Smooth highly-textured polycrystalline GaN films were grown on the *in situ* cleaned GaN substrates and the effects of NH_3 kinetic energy on growth rate and film morphology were examined. The growth are summarized in Table II.

Table II. GaN Films Grown at 700°C Using a 950°C Ga K-cell

Film	Growth Time (hr)	% NH_3	NH_3 Kinetic Energy (eV)	Growth Rate (nm)	RMS Roughness (nm)
1	2	23%	0.25	90	7.5
2	2	10%	0.33	109	7.1
3	4	10%	0.33	114	4.8
4	4	10%	0.61	105	3.3

The growth rate does not change within experimental uncertainty for the 3 films grown using 10% NH_3 beams. The results indicate, however, the film roughness decreases with increasing NH_3 kinetic energy and film thickness. The film grown using a 0.61 eV NH_3 beam has a smooth surface exhibiting hexagonal plates, as seen in the AFM image in Fig. 3. We infer from the image that the epitaxial film consists of a mosaic of (0001)-oriented GaN domains.

Contamination of Surface and Film. Growth of films at 700°C with a 10% / 0.61 eV NH_3 was repeated resulting in a rough highly-faceted film as shown Fig. 4. This film was grown following a maintenance shutdown of the SEE system.

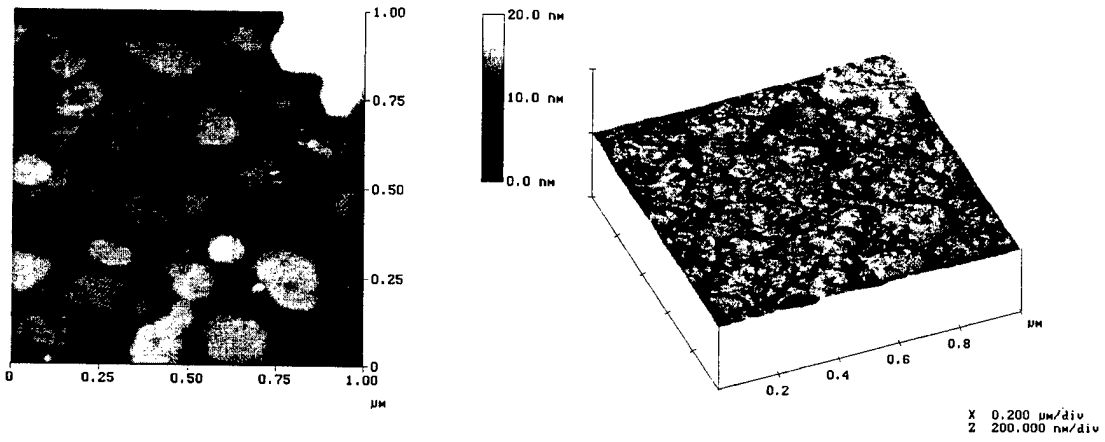


Figure 3. AFM images of GaN film; grown at 700°C with 0.61 eV NH_3 beam and 950°C Ga K-cell.

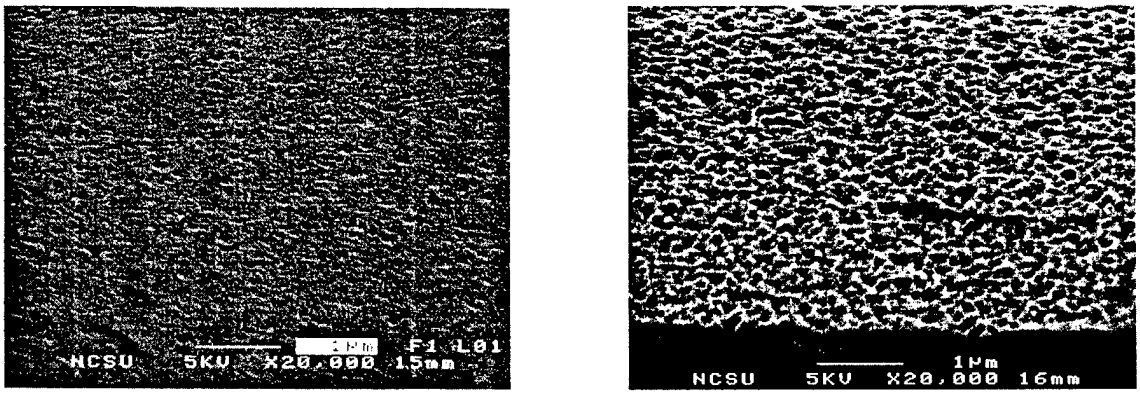


Figure 4. SEM comparison of films grown under identical conditions showing the effect of contamination on growth morphology.

We infer that the rough films result from contaminants adsorption from the vacuum ambient during cleaning and/or growth. A clean surface allows epitaxial growth to begin at steps. With a contaminated surface, the GaN nucleates at surface contamination sites and grows in three dimensional pyramids. We are currently doing a check of our system to identify and eliminate sources of contamination. The previous report mentioned a Si contamination problem, as evidenced by SIMS. QMS indicated that there was no silicon contamination coming from the source chamber through the nozzles. There is also no silicon contamination source in the deposition chamber. It was recently discovered that the apparent silicon contamination problem may be due to SIMS measurement error. The problem is being corrected, and new SIMS analyses of our films are currently being done.

E. Future Plans

The carbon and oxygen contamination sources will identified and eliminated. In order to facilitate removal of surface contamination, supersonic Kr seeded in He will be fed through a second nozzle during NH_3 beam cleaning. The kinetic energy of the neutral Kr should help to remove surface contaminants while keeping the substrate temperature below that of GaN decomposition. RHEED and AFM of the substrate will be done to ensure that energetic Kr does not damage the smooth stepped surface. XPS of the films will be done to determine percent contamination.

RF nitrogen plasma cleaning is also being examined for *in situ* carbon removal. These experiments are done in a separate plasma chamber equipped with AES and LEED analysis capabilities to measure the plasma effect on surface contaminant removal and surface morphology. These experiments will be done in cooperation with the ASU group since they are studying N plasma cleaning of GaN substrates using LEEM.

Once it is determined that *in situ* cleaning produces clean substrates, a more detailed investigation of GaN homoepitaxial growth using dual NH_3 and TEG supersonic beams will be done to elucidate the relationships between film quality and precursor kinetic energies tuned by seeded supersonic beams. Results from the growth of relatively smooth films using the Ga K-cell will be used to estimate the Ga flux needed to grow smooth films using a supersonic TEG beam. Comparisons will be made between the NH_3 kinetic energy effect on growth rate and film morphology and TEG kinetic effects.

Time of flight (TOF) velocity measurements will be made in order to establish velocity and kinetic energy distributions of the seeded supersonic molecular beams.

A radio-frequency discharge nozzle/nitrogen atom source [5,6] will be constructed and installed in the system. This source will produce a supersonic beam of atomic nitrogen and will be used in conjunction with the TEG supersonic source and the Ga effusion cell for GaN growth.

Real-time RHEED intensity measurements will be used to investigate the growth mode of GaN epilayers. In the short term, a photomultiplier tube will be mounted in front of the RHEED screen to monitor the intensity of the specular beam. Long-term plans include a CCD camera based RHEED data acquisition system.

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